Catalytic Chemistry in Supercritical Fluids

Over 90% of industrial chemical processes entail the use of catalysts, and nearly half of these are homogeneous catalytic processes in which the catalyst is dissolved in a fluid. We have pioneered in research investigating catalytic reactions in supercritical fluids.

Supercritical fluids such as CO_2 and water offer inexpensive and environmentally benign alternatives to the toxic organic solvents that are commonly used in homogeneous catalysis. An additional advantage is the elimination of energy-intensive distillations necessary for product separations and catalyst recovery from organic solvents. Our recent research has focused on the development of phosphine-modified cobalt catalysts for the hydroformylation of olefins in supercritical CO_2.

The hydroformylation of olefins, also known as the oxo reaction, is the largest industrial process that is catalyzed by homogeneous catalysts. This process, which is usually conducted in organic media, converts olefins to aldehydes, as exemplified with ethylene:

$$C_2H_4 + CO + H_2 \rightleftharpoons CH_3CH_2CHO$$

While rhodium catalysts account for most of the C_4 hydroformylation products, oxo reactions producing C_5 and higher products are dominated by cobalt over rhodium catalysts by a ratio of 9 to 1. The primary advantage of cobalt catalysts is their higher reactivity toward internal olefins. The phosphine-modified cobalt catalyst process, which was discovered and is used exclusively by Shell Chemical Co., differs from the unmodified cobalt carbonyl catalyst $Co_2(CO)_8$ in that the presence of a tertiary phosphine improves the selectivity toward the linear products. Our interest in Shell's hydroformylation process stems from its industrial importance and the fact that the phosphine ligand provides for easy modification to produce cobalt catalysts that are soluble in supercritical CO_2.

In our earlier study of Shell's phosphine-modified cobalt catalyst system with tributylphosphine in organic solvents, we discovered that $[Co(PBu_3)_2(CO)_3][Co(CO)_4]$ was produced under the oxo reaction conditions according to

$$Co_2(PBu_3)_2(CO)_6 + CO \rightleftharpoons Co(PBu_3)_2(CO)_3^+ + Co(CO)_4^-$$

The reaction reduces the concentration of $Co_2(PBu_3)_2(CO)_6$, and, therefore, the concentration of the key hydride intermediate, $HCo(PBu_3)(CO)_3$. This intermediate species is generated from $Co_2(PBu_3)_2(CO)_6$ as follows:

$$Co_2(PBu_3)_2(CO)_6 + H_2 \rightleftharpoons 2HCo(PBu_3)(CO)_3$$

This salt formation presented a particular challenge for the development of supercritical CO_2 as a solvent for the phosphine-modified hydroformylation reaction since this supercritical fluid is known to be a poor solvent for salts. We found that all of the cobalt species precipitated from supercritical CO_2 using highly basic phosphines, such as PBu_3.

We approached this problem by fine tuning the phosphine ligand to decrease the basicity with the goal of reducing the driving force for salt formation. Furthermore, the use of fluorine substituents had the additional advantage of enhancing the solubility of the cobalt complexes in supercritical CO_2. Accordingly, we have synthesized $Co_2[P(C_6H_4CF_3)_3]_2(CO)_6$ and showed that it catalyzes the hydroformylation of ethylene (see first reaction above) in supercritical CO_2 with a rate comparable to that of the unsubstituted cobalt carbonyl catalyst. A great surprise was the discovery that with a 1:1 ratio of CO/H_2 gas, this catalyst continued to function until all the CO/H_2 was consumed, as shown by the curve so labeled in the figure below. For comparison, this figure also shows the curve obtained for the consumption of H_2 with the unsubstituted $Co_2(CO)_8$ under similar conditions. This reaction stopped when the CO pressure (the same as H_2) reached 4.5 atm, because of decomposition of the catalyst. The presence of the $P(C_6H_4CF_3)_3$ ligand apparently stabilizes the catalyst at 100ºC without the need of a CO pressure.

We have thus shown that $P(C_6H_4CF_3)_3$- substituted cobalt carbonyl catalyst is active in catalyzing the hydroformylation of ethylene. The results further show that the hydroformylation reaction may be carried out at atmospheric pressure. For practical consideration, it is desirable to carry out the reaction at moderate pressures to reduce capital equipment costs. The main advantage for this catalyst is that the reaction may be carried out until all the CO and H_2 are used up, eliminating the need to recycle these gaseous reactants. At the end of the reaction, all that is required is to isolate the products from supercritical CO_2, a very simple process.

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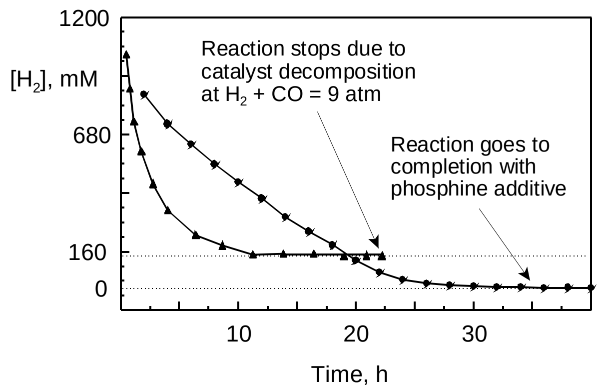

Rate Plots for the Hydroformylation of Ethylene with and without Phosphine Additive

Test conditions: 100ºC, $[H_2] = [CO] = 1.1\ \underline{M}$, $[C_2H_4] = 2.0\ \underline{M}$, and CO_2 partial pressure = 119 atm. Triangles indicate $[Co_2(CO)_8] = 4.1\ m\underline{M}$; circles, $[Co_2(CO)_6L_2] = 4.1\ m\underline{M}$ and $P(C_6H_4CF_3)_3 = 74\ m\underline{M}$.